National Aeronautics and Space Administration

Ionic Liquid Facilitated Recovery of Metals and Oxygen from Regolith

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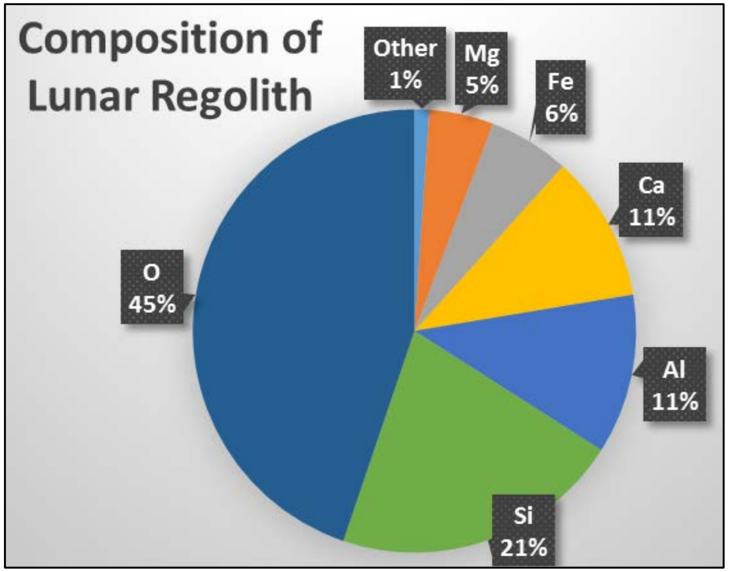
What does Regolith Offer?

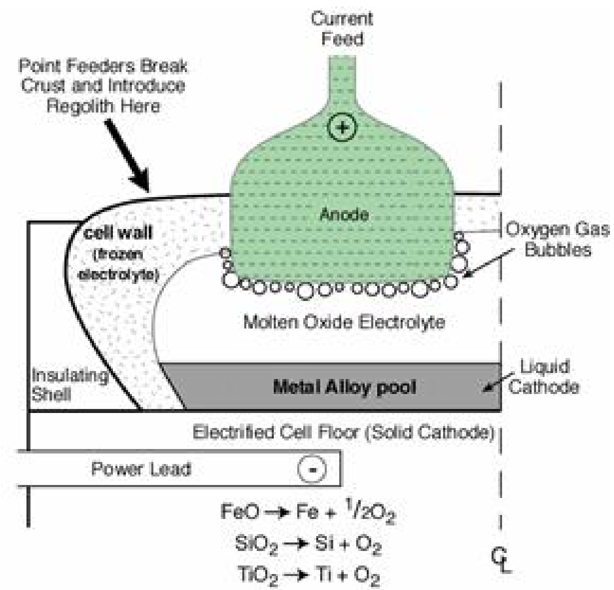


- In-space manufacturing is a promising route to reduce the launch mass of deep space exploration missions.
- However, these processes still require feedstock.
- Producing these feedstocks from in situ resources (in situ resource utilization or ISRU) further reduces the mass launch required for these missions
- Martian and lunar regolith contain valuable elements for many applications such as:
  - Fe and Mg for aerospace applications
  - Si for solar cells
  - Na or Mg for the preparation of binders for cement like materials
  - Oxygen for life support or propellant
- However, rather than being found in their elemental form, these materials are found in highly stable oxides.
- Processing these oxides to recover high purity materials is technically challenging.

Oxide Processing Techniques

- Terrestrial mining technology to recover metals from metals oxides is very mature.
- Processes generally use large volumes of chemicals which are often caustic or corrosive or thermal methods which require high energy inputs.

- NASA has studied molten oxide electrolysis (MOE) as a potentially space suitable approach to recovering metals from metal oxides.
- MOE works, but requires high temperatures (1400 – 2000 °C), so energy inputs are high. Additionally, these high temperatures impose significant material compatibility limitations.



MOE furnace during plating.

What are Ionic Liquids?

- Ionic liquids (IL) are organic salts which are molten at or near room temperature.
- Being entirely composed of ions, ILs have a number of properties that make them attractive for in-space use, including high electrochemical and thermal stability, low vapor pressure, and high ionic conductivity.
- The chemical structure of ILs can be readily modified through simple chemical processes, which allows for the preparation of task specific ILs, or ILs with properties tuned for a given application.
- ILs are potentially useful in a number of NASA relevant applications, including environmental control and life support, advanced manufacturing, in situ resource utilization, and propulsion.
- Select ILs have been shown to chemical digest many metal oxides.

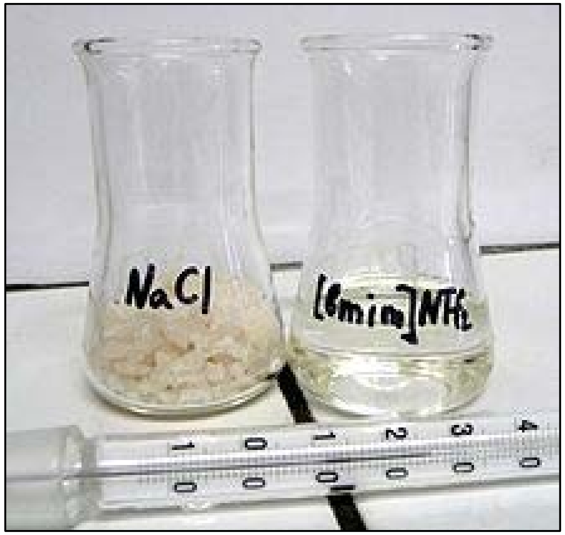
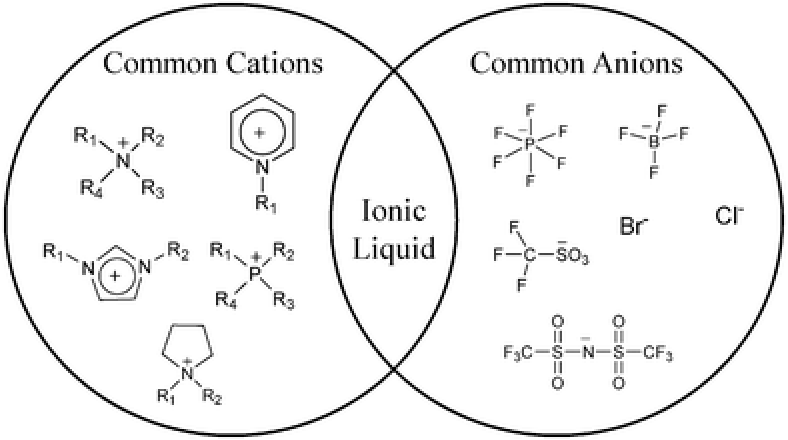


Table salt (left) and an IL (right).



M.D. Joshi and J. L. Anderson RSC Adv., 2, 5470–5484 (2012).

The Process

- A three step process that uses ILs to digest regolith and recover high purity metals has been demonstrated.
- First, an acidic IL is used to digest the metal oxide producing a solution of dissolved metal in depleted IL and water as a byproduct.

$$2HSO_4^- + MO \rightarrow 2SO_4^{2-} + M^{2+} + H_2O$$

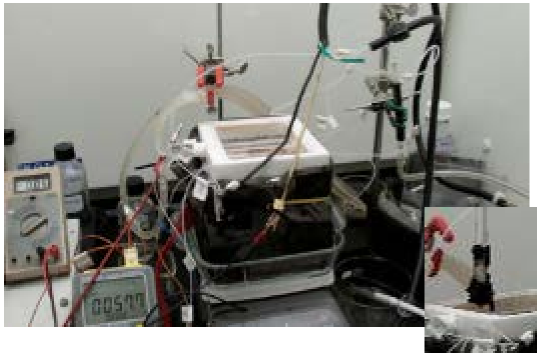
- The water produced in the first step is electrolyzed and the H_2 produced is stored for use in the third step.
- The dissolved metals are electrochemically plated out of solution while the depleted IL is regenerated to its acidic state.

$$M^{2+} + 2e^- \rightarrow M \;||\; 2SO_4^{2-} + H_2 \rightarrow 2HSO_4^- + 2e^-$$

- The IL is then ready for reuse to digest additional regolith.

Regolith Digestion

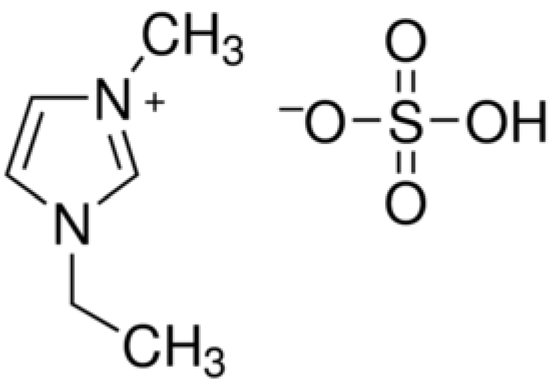
Water Electrolysis



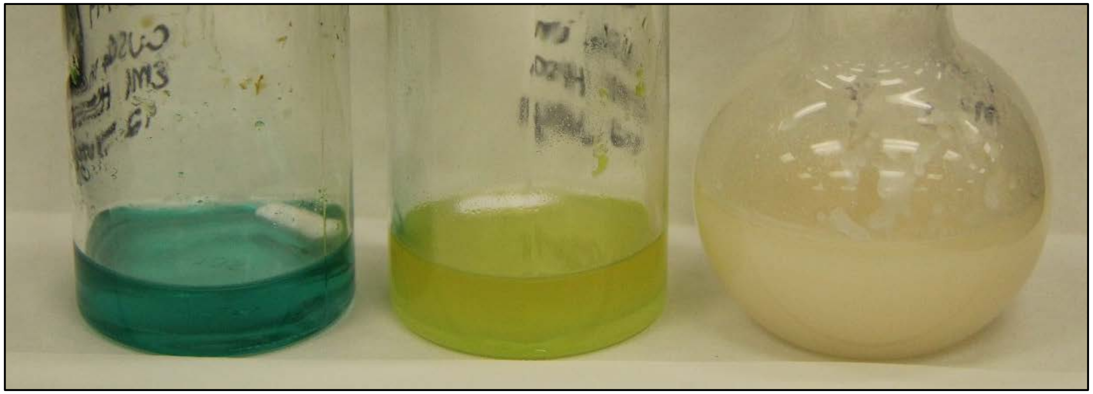
Metals Plating and IL Regeneration

Digestion of Metal Oxides

- There are many “acidic” ILs available.
- 1-ethyl-3-methylimidazolium hydrogensulfate (EMI HSO_4) was the primary IL used for this work.
- Offers a good balance of fluidity, electrochemical stability, chemical reactivity, and vapor pressure.
- EMI HSO_4 has successfully digested Fe and Mg oxides, as well as Ni metal.
- Other ILs have been identified to partially digest feldspar and to fully digest TiO_2 at 200 °C.
- No ILs have been able to completely digest SiO_2 and no work has been performed with CaO.



EMI HSO_4



Solution of EMI HSO_4 and 0.1 M Copper (left), nickel (middle), and magnesium.

Metals Electroplating

Table of Standard Electrochemical Potentials for Regolith Processing

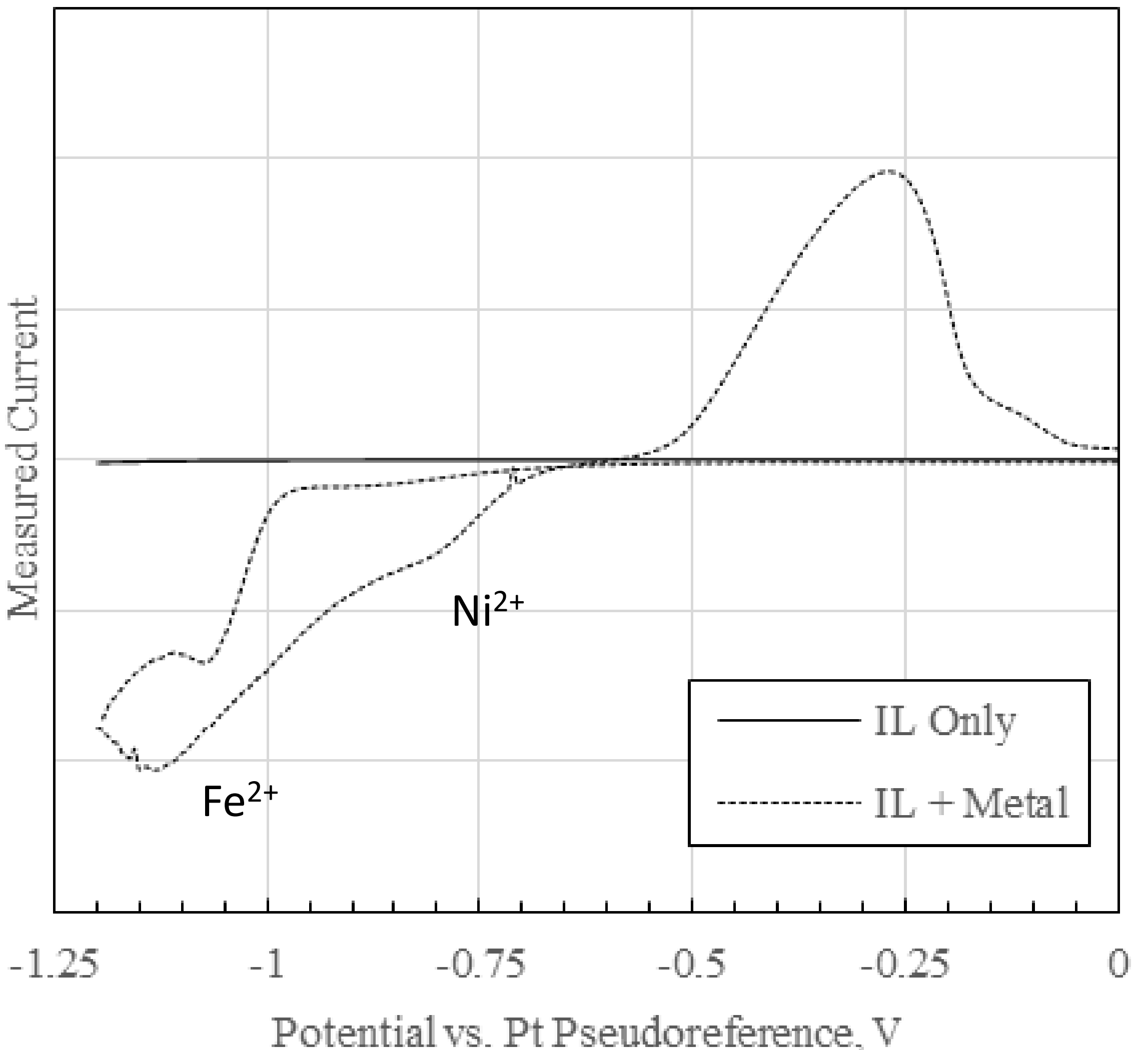
Increasing Electropositivity

Oxidant		Reductant	E°(V) vs. SHE
$Ni^{2+} + 2e^-$	$\leftrightarrow$	Ni	-0.25
$Fe^{2+} + 2e^-$	$\leftrightarrow$	Fe	-0.44
$Ti^{2+} + 2e^-$	$\leftrightarrow$	Ti	-1.63
$Al^{3+} + 3e^-$	$\leftrightarrow$	Al	-1.662
$Mg^{2+} + 2e^-$	$\leftrightarrow$	Mg	-2.372
$Ca^{2+} + 2e^-$	$\leftrightarrow$	Ca	-2.868

Limit of aqueous solutions

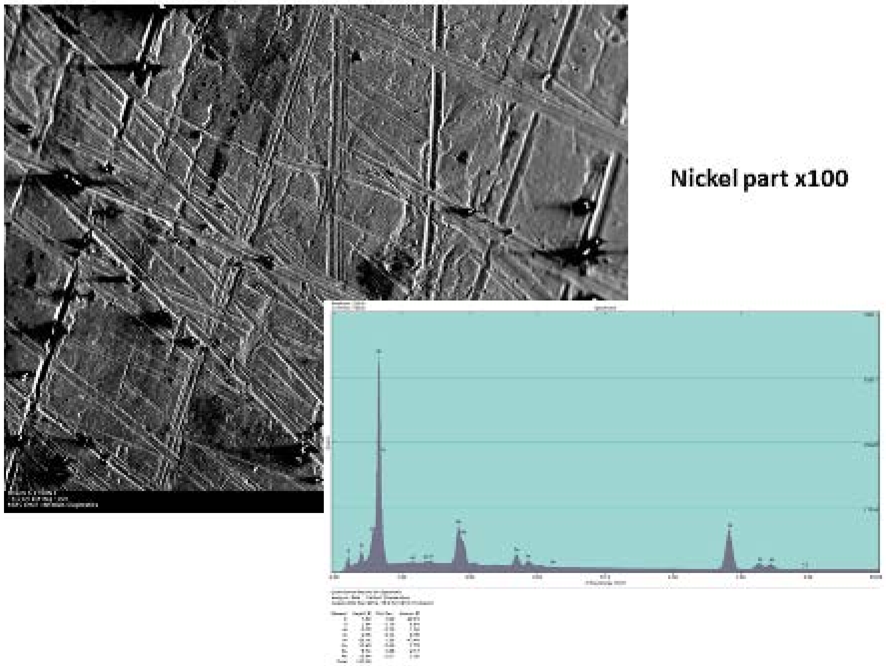
- Sequential application of increasing reduction potential allows for the recovery of single elements from the solution.
- Recovering N elements would require N + 1 electrodes, where the extra electrode would be used to plate out all dissolved species that were less electropositive than the targeted metal.
- Aqueous mineral acids solutions only allow for the recovery of Fe and Ni, as water begins to electrolyze at -1.23 V.
- The large electrochemical windows of ILs allow for the recovery of highly electropositive elements such as Mg.
- pH measurement of the plating solutions show a change from 4, representing the depleted IL solution, to 2, indicating that the IL is fully regenerated.

Recovery of Single Metals



- 0.05 M solution of metal in IL
- 93% Fe, 7% Ni (m/m)
- Typical of a Ni-Fe meteorite
- Ni reduces around -0.8 V and Fe reduces around -1.0 V
- Peak assignments were verified by single element CV

Recovery of Single Metals

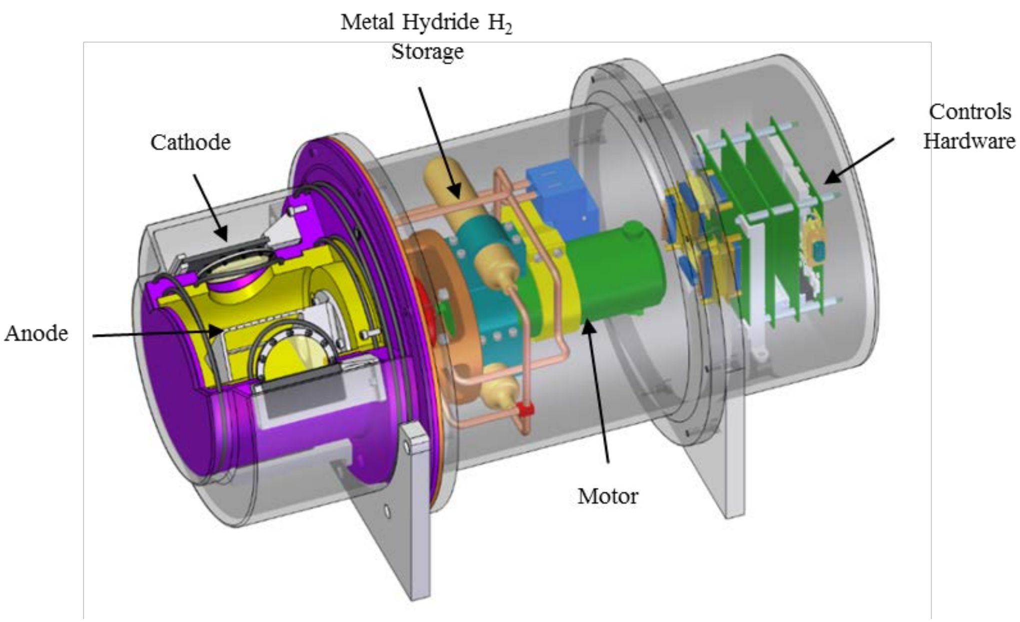


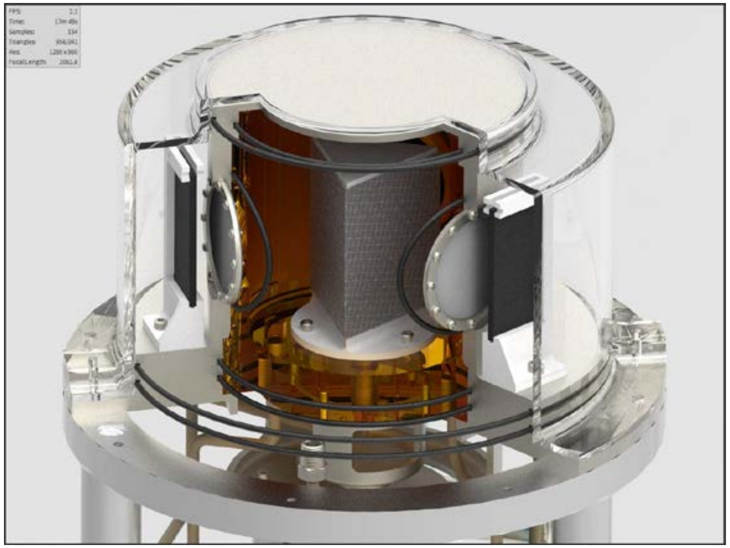
SEM micrograph and SEM EDS analysis of electroplated metals.

Water recovered from IL after digestion of Asteroid Vesta material.

- Electroplating of Fe-Ni solutions resulted in the recovery of single elements with purity greater than 99%.
- The water byproduct from the metal oxide digestion was successfully recovered through vacuum distillation.

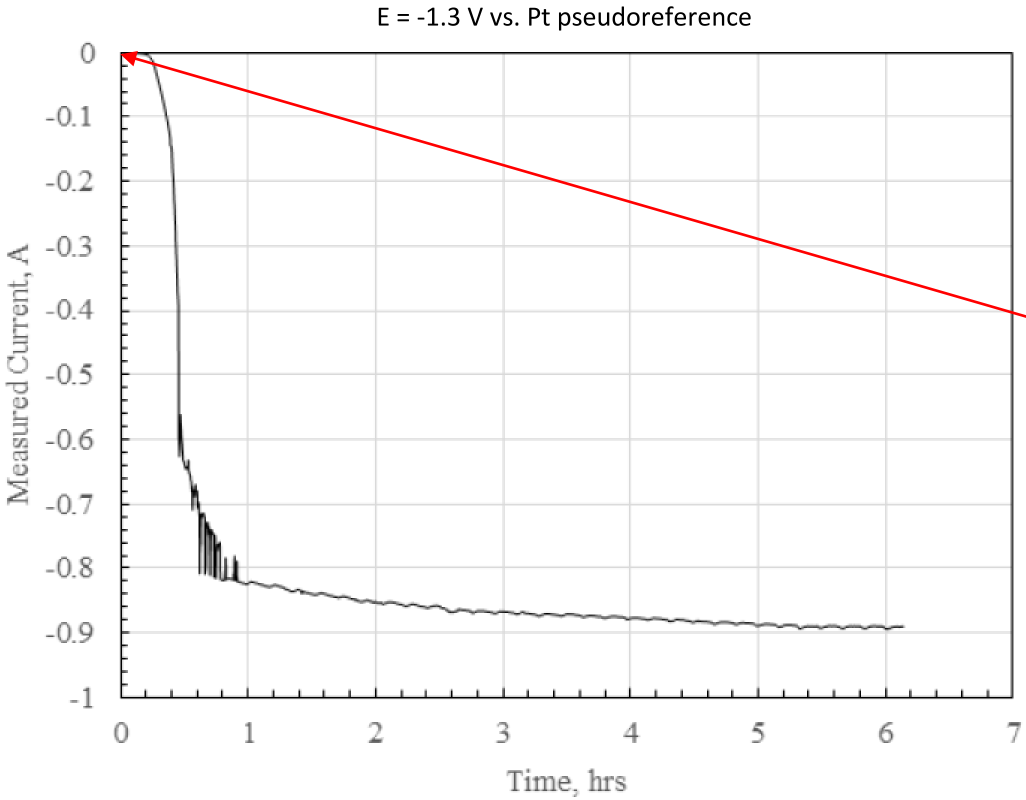
Engineering Development Unit

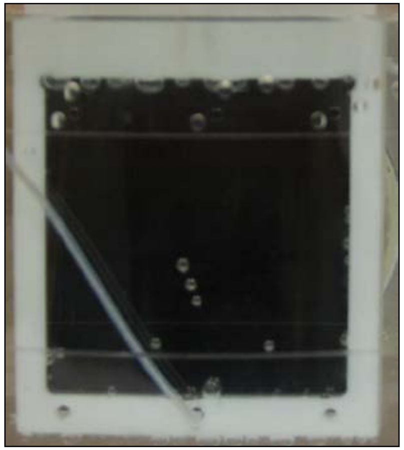




- An Engineering Development Unit was fabricated to allow for the refinement of the design of flight hardware for experiments in microgravity.
- Contains three electrodes to recover Ni and Fe.
- Fully isolatable anolyte chamber prevents regenerated IL from digested plated material
- Work is ongoing to refine the fully autonomous control systems and electrochemical regime.

Bulk Electroplating

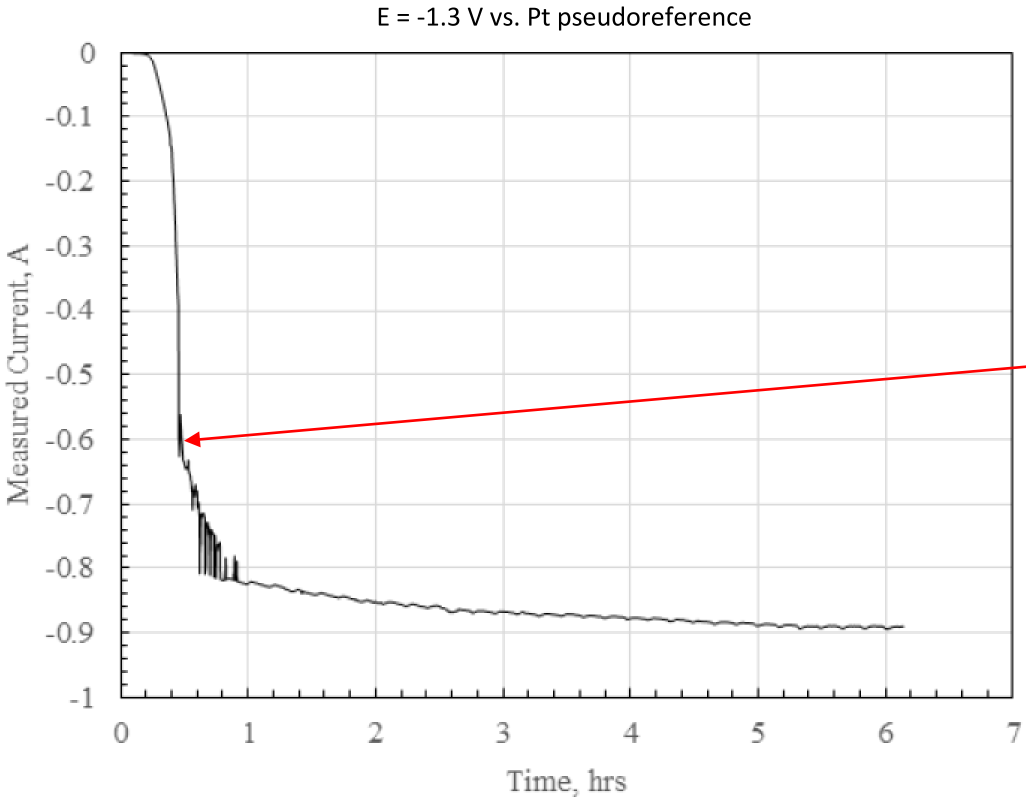


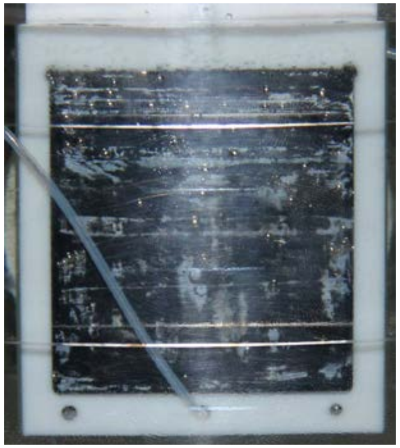


Glassy carbon electrode at t = 0 min

- Electrolyte was a solution of 0.1 M EMI HSO_4 and 0.05 M metal (93% Fe, 7% Ni) in water.
- Initial testing at -0.95 V targeting Ni recovery resulted in no current and the lack of metal deposition was confirmed by SEM EDS.
- Increasing the applied reduction potential to -1.3 V produced a small current of 1 mA.

Bulk Electroplating

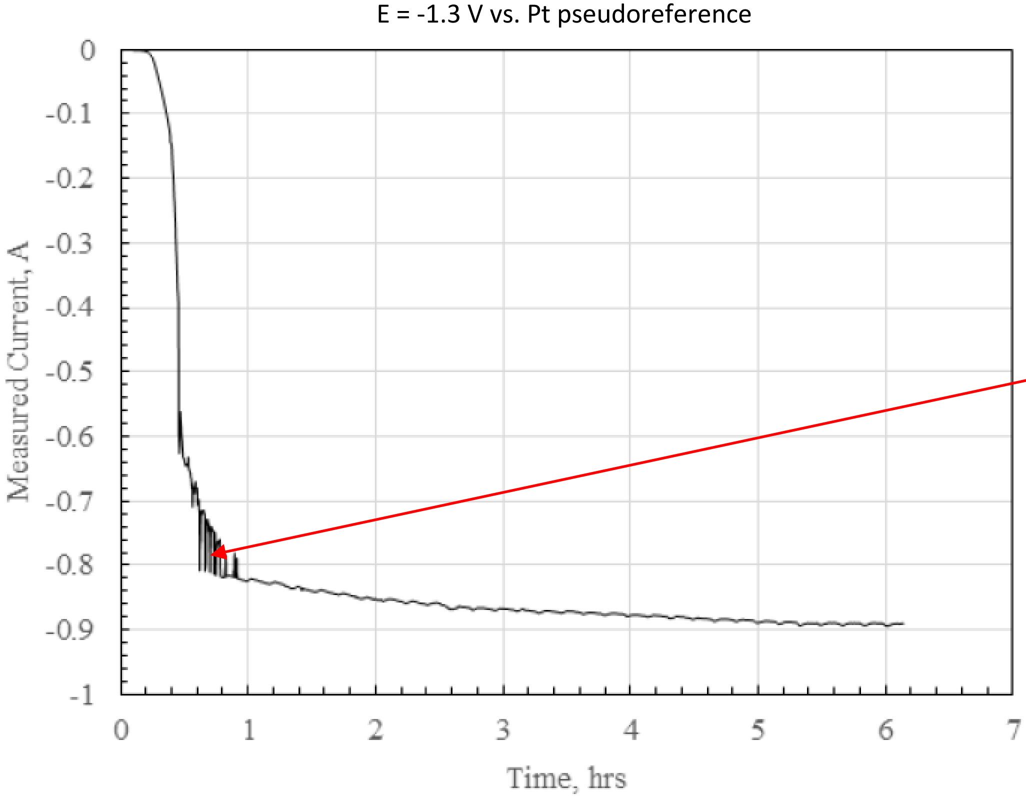


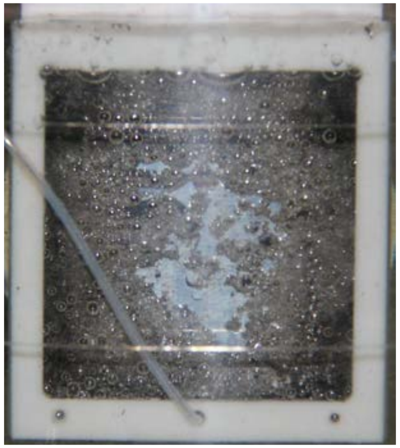


Glassy carbon electrode at t = 25 min

- At approximately 20 min, the measured current started a rapid increase.
- This corresponded to the appearance of metal deposits on the surface of the electrode.

Bulk Electroplating

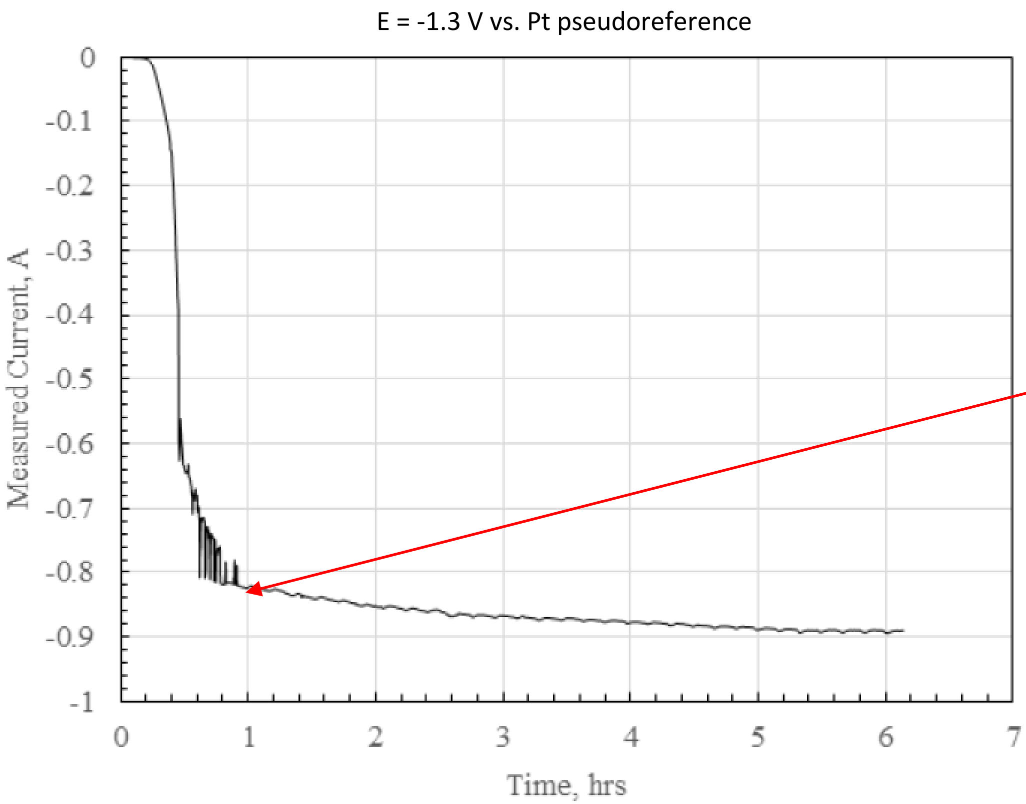




Glassy carbon electrode at t = 35 min

- The electrode was almost entirely covered with deposited metal.
- The fluctuations in current are the result of metal flakes forming and detaching from the electrode resulting significant surface area changes.
- Bubbles are from the hydrolysis of water

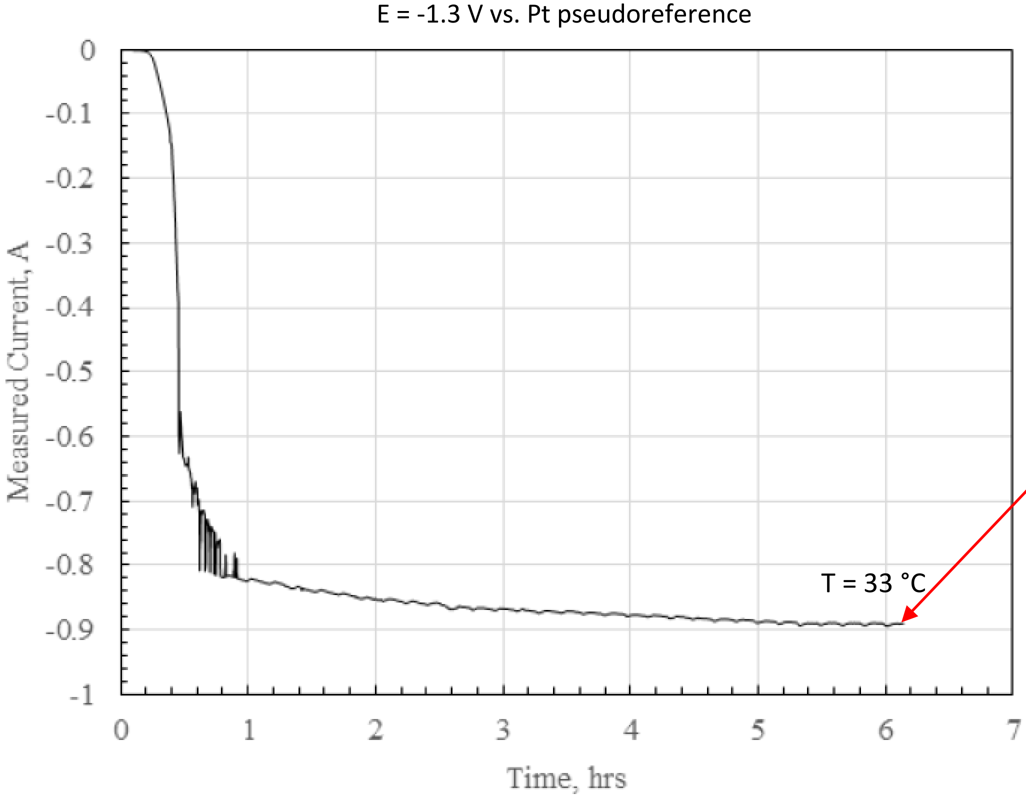
Bulk Electroplating

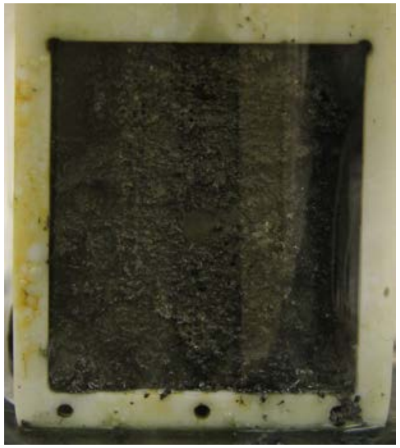


Glassy carbon electrode at t = 55 min

- The electrode surface area was entirely covered with deposited metal.

Bulk Electroplating

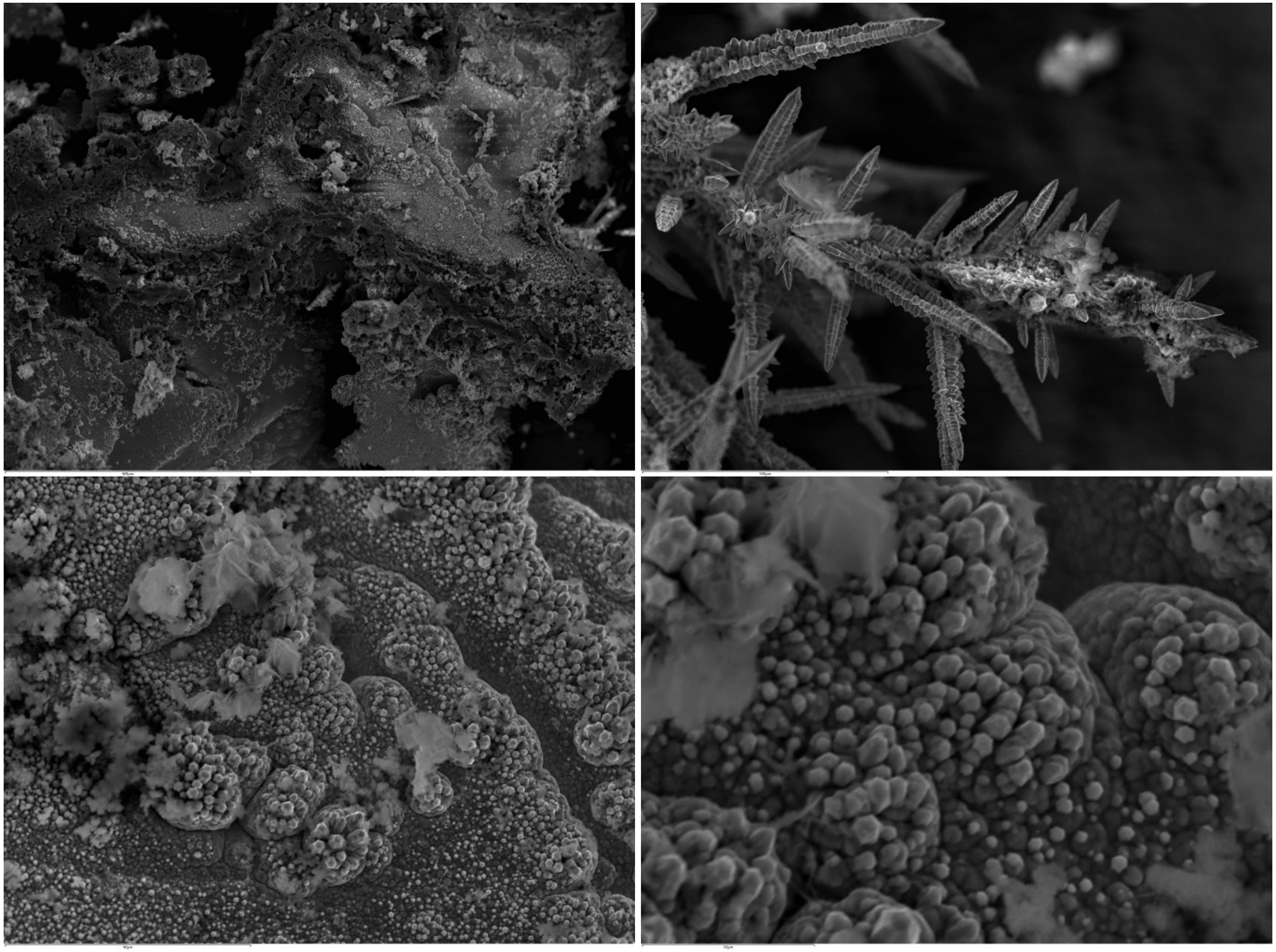




Glassy carbon electrode at t = 375 min

- The experiment was terminated after approximately 6 hours of runtime due to an increasingly rapid temperature rise. This was the result of the exothermic absorption of H_2 onto the Pt black anode and resistive heating of the electrolyte.
- Analysis of the total charge suggests half of the dissolved material was recovered.

Bulk Electroplating



- SEM EDS indicated that the deposited metal had an identical composition as the original dissolved metals.

Summary

- An IL-based process that allows for the digestion of regolith and recovery of metals and oxygen has been demonstrated.
- The process is 100% closed loop in regards to chemical reagents, requiring only energy and regolith inputs.
- High purity metals have been recovered from binary solutions.
- ILs have been identified to chemically process the majority of the metal oxides found in martian and lunar regolith.
- The development of hardware for an eventual flight experiment is ongoing.
- Further refinement of the electrochemical regime and hardware is required.